

TIMING OF FORMATION OF A WASSONITE-BEARING CHONDRULE. A. W. Needham^{1,2}, K. Nakamura-Messenger², A. E. Rubin³, B.-G. Choi⁴, and S. Messenger². ¹Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058, USA. E-mail: andrew.w.needham@nasa.gov. ²Robert M. Walker Laboratory for Space Science, ARES, NASA JSC, 2101 NASA Parkway, Houston TX 77058, USA. ³Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90095-1567, U.S.A. ⁴Earth Science Education, Seoul National University, Seoul 151-748, South Korea.

Introduction: Wassonite, ideally stoichiometric TiS, is a titanium monosulfide recently discovered in the Yamato 691 EH3 enstatite chondrite [1]. Wassonite grains were located within the mesostasis of a single barred olivine chondrule. Such chondrules likely formed in the solar nebula by melting of fine grained precursor dust [e.g. 2,3]. The reduced nature of enstatite chondrites, and the wassonite-bearing chondrule in particular, may suggest precursor materials included Ti-bearing troilite, metallic Fe-Ni, and possibly graphite. Under the reducing conditions present in enstatite chondrites S can partition more readily into silicate melt [4,5,6], leading to raised Ti content of the residual Fe-FeS melt. By the time sulfide crystallized from the melt, the Ti concentration was high enough to form small grains of pure TiS - wassonite.

As a mineral not previously observed in nature wassonite and its host chondrule may provide additional constraints on physical and chemical conditions in the solar nebula at a specific time and location relevant to planetary formation. Enstatite chondrites and Earth share similar isotopic compositions of Cr, Ni, Ti, O and N [e.g. 7,8]. Understanding the formation conditions of enstatite chondrite chondrules may therefore have wider relevance for terrestrial planet accretion and other early inner solar system processes.

Here we present preliminary results of an investigation of the Al-Mg systematics of the only known wassonite-bearing chondrule. The goal of this study is to determine whether this chondrule's formation was contemporaneous with other enstatite chondrite chondrules and to establish its place in the broader timeline of solar system events.

Sample description: The host chondrule (Fig. 1), located within thin section 79-1 of Y691, is a 72 μm diameter barred olivine chondrule containing magnesian olivine (Fa 0.7) and a feldspathic, moderately sodic mesostasis. Wassonite grains, all less than 0.5 μm in diameter, occur within the mesostasis. Full mineralogical details are reported by [1].

Methods: Prior to isotopic analyses the chondrule and surrounding area was mapped with a JEOL 7600F field-emission scanning electron microscope. Electron backscatter and energy-dispersive X-ray (EDX) maps were obtained at sub- μm per pixel resolution to locate regions with high Al/Mg ratios. Mg isotopic analyses were then conducted using the JSC NanoSIMS 50L ion

microprobe. Positive isotopic images of $^{24,25,26}\text{Mg}$, ^{27}Al , and a combination of ^{12}C , ^{23}Na , ^{28}Si , ^{40}Ca and ^{48}Ti were acquired in several analytical sessions. Images were acquired in multidetection, from 5-10 μm fields of view, with electron multipliers. The images were acquired using a 1-8 pA O_2^- primary ion beam with a spatial resolution of ~300-600 nm. Regions of interest within the images having a range of Al/Mg ratios were defined from the $^{27}\text{Al}/^{24}\text{Mg}$ ratio images. We then determined Al/Mg and Mg isotopic ratios for these regions. The data were normalized to San Carlos olivine and spinel standards. Feldspars and volcanic glasses covering a wide range of Al/Mg ratios were analyzed in the same analytical sessions. From these and previously reported measurements [9] we applied a relative sensitivity factor of 1.34 to correct the measured Al/Mg ratios.

Results: A subset of Al-rich, Mg-poor regions of the chondrule mesostasis identified in EDX maps were chosen for isotopic analysis. The Al-rich regions ranged in size from 0.5 – 3 μm . The small sizes of these target areas limited the achievable statistical precision of the Mg isotopic measurements. However, this was ameliorated by the sub- μm spatial resolution of the NanoSIMS images that enabled good resolution of Mg- and Al-rich regions. $^{27}\text{Al}/^{24}\text{Mg}$ ratios of up to 100 were identified in the isotopic images.

Mg isotopic data for the Mg-rich portions of the wassonite-bearing chondrule were within 2 per mil error of terrestrial standards in all analyses. All data for the Al-rich regions were therefore referenced to the Mg-rich sub-regions within each image. No evidence was found for excess ^{26}Mg within analytical error. Confidence limits on the analyses place an upper limit of 1.7×10^{-5} initial $^{26}\text{Al}/^{27}\text{Al}$ (Fig. 2), suggesting formation ages of at least 1.1 Ma after most CAIs.

Discussion: Al-Mg systematics are susceptible to parent-body processes and the effects of terrestrial weathering. Yamato 691 was discovered in Antarctica and thus has had a long terrestrial residence time. However, fine grained nebular components are preserved and phyllosilicates are largely absent [10]. As a type-3 chondrite, Y691 has experienced little parent-body heating, and attempts to characterize a finer scale of petrologic types based on Cr contents of olivine, a sensitive indicator of heating in other chondrite groups

[11], are hampered by the influence of reduction process in enstatite chondrites [12]. For the purposes of this study we therefore assume that the low degrees of weathering and parent-body alteration have not affected the Mg isotopic composition of the mesostasis.

The derived upper limit of initial $^{26}\text{Al}/^{27}\text{Al}$ of 1.7×10^{-5} is consistent with previous Al-Mg analyses of chondrules that have typically been found to have initial $^{26}\text{Al}/^{27}\text{Al}$ ratios below the canonical initial solar system value defined by CAIs. In situ Al-Mg measurements of unequilibrated ordinary chondrites and carbonaceous chondrites find most chondrules to have initial $^{26}\text{Al}/^{27}\text{Al}$ ratios of $\sim 0.5 - 2 \times 10^{-5}$ [13,14,15]. Few data exist for chondrules in enstatite chondrites.

The enstatite chondrites formed in a more reducing environment than other chondrite groups, and the mineral phases present within the wassonite-bearing chondrule demonstrate unique conditions of its formation. Similarly, evidence exists for variations in redox conditions during the formation of single CAIs and their rims [16]. This indicates large-scale variations in chemical reservoirs in the early solar system. The heterogeneous redox conditions of these reservoirs are currently poorly constrained. Additional information, such as the discovery of wassonite, may prove valuable in constraining at least some aspects of variable solar nebula redox conditions – such as the evolution of reservoirs with time. The data presented here suggest contemporaneous formation with other chondrules.

Conclusion and future work: The wassonite-bearing chondrule experienced hitherto unobserved formation conditions. Close isotopic links between enstatite chondrites and the Earth [e.g., 7,8] indicate formation in a well-mixed region of the inner solar system. The wassonite-bearing chondrule may therefore represent either local physico-chemical variations in the enstatite-chondrite chondrule-forming region, or a distinct population of chondrules only rarely sampled by the accreting enstatite chondrite parent bodies. Mg isotope data presented here suggest formation ages at least 1.1 Ma after the first CAIs, providing at least one fundamental constraint that these reducing conditions were not the result of early formation.

Future O-isotope analyses may further constrain the origin of this unique chondrule in terms of nebula location/isotopic reservoir.

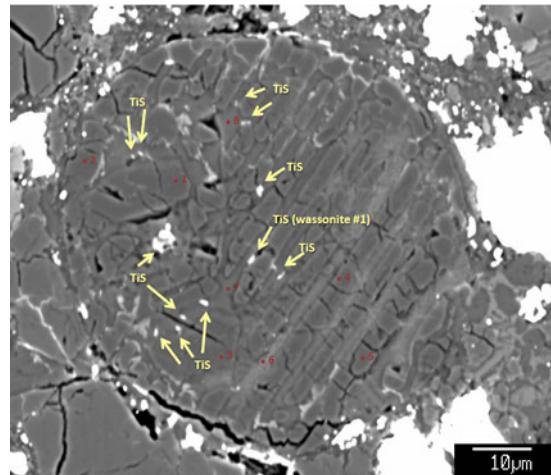


Fig 1: BSE image of chondrule 79-1. Arrows show wassonite locations

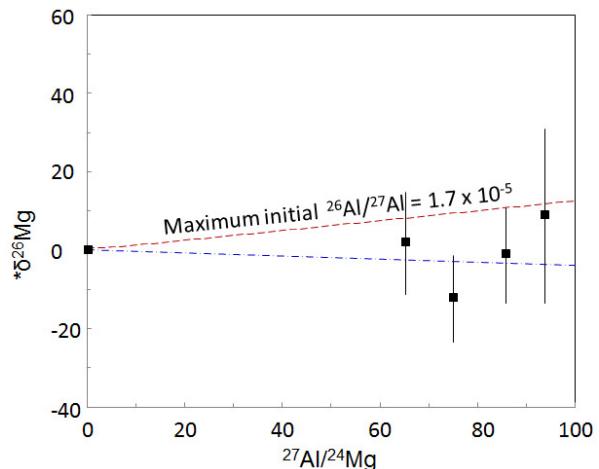


Fig 2: Al-Mg diagram of the wassonite-bearing chondrule. A maximum initial $^{26}\text{Al}/^{27}\text{Al}$ ratio indicates formation at least 1.1 Ma after the first CAIs formed.

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